

PATENT SPECIFICATION

(11) 1438203

- 203 (21) Application No. 35423/74 (22) Filed 29 July 1974
 202 (31) Convention Application No. TE 733 (32) Filed 2 Aug. 1973 in
 201 (33) Hungary (HU)
 1438 (44) Complete Specification published 3 June 1976
 200 (51) INT CL² H01M 10/44//12/08
 143 (52) Index at acceptance
 1 H1B 1044 1208 202 490 492



(54) METAL-AIR HYBRID FUEL CELL

(71) We, INTERAG R. T. and TEX-ELEKTRA TEXTIL- ÉS ELEKTRONIKA IPARI SZÖVETKEZET, both bodies corporate organized under the laws of Hungary, of 11 Rajik Laszlo utca, Budapest XIII and 19 Béke tér, Budaörs, Hungary, respectively, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a metal-air hybrid fuel cell comprising a metal anode, an oxygen-operated cathode provided with a catalyst layer, and an acidic or alkaline electrolyte.

It is known that metal-air hybrid fuel cells comprising a hydrophobic oxygen electrode can be charged internally or externally. Internal charging can be accomplished directly for those oxygen electrodes where the catalyst remains chemically unchanged during the process. Such a catalyst is, for example, platinum. For other catalysts, e.g. silver, the cell can be charged only with a so-called auxiliary electrode which ensures that the potential at the oxygen electrode remains zero. Otherwise silver would be converted into silver-oxide, thereby changing the structure of the electrode and rendering it ineffective.

A serious disadvantage of internal charging is that the life of the oxygen electrode is shortened regardless of the nature of the catalyst.

In the case of external charging the discharged metal electrode is removed from the cell, charged in a suitable equipment, and then reinstalled into the cell, whereupon the cell becomes operable again. A disadvantage of external charging is that, owing to the large amount of alkali in the metal electrode and the separator, the removal of the metal electrode, e.g. zinc electrode, causes a substantial alkali loss. A further disadvantage is that the recharging process is complicated, since it requires additional fittings, e.g. vats. The main disadvantage of this method is, however, that the repeated removal and re-

installation physically exhausts the metal electrode, gradually reducing its strength and finally causing the metal electrode to crumble.

The known metal-air hybrid fuel cells are arranged so that their cathode forms simultaneously the outer casing of the cell, while the anode(s) is or are arranged in the inner space formed by the cathode. This arrangement takes advantage of the fact that the cathode, being hydrophobic, prevents leaking of the alkali, but is permeable to air. Consequently, when several cells are to be built together to form a larger unit or a battery, a suitable distance must be left between the individual cells to ensure an adequate air or oxygen supply for the cathode. Under more intense loading (over about 100 mA/cm²) the nitrogen liberated in use from the operating cell is removed with the aid of a ventilator in order to provide an adequate oxygen supply.

The use of the cathode as the cell casing involves several disadvantages, the most serious of which are as follows:

a) During operation alkali may pass through the cathode, resulting in a slight oozing. Other failures in sealing may also frequently cause the alkali to escape, leading to a rapid decrease in the alkali level. This phenomenon is accelerated by the fact that the cathode-anode distance is very small, about 1 mm., and therefore the amount of alkali between the electrodes is very low. As a consequence, the metal electrode is in contact directly with the oxygen of the air, and oxidizes, i.e. discharges without having actually been used. Thus a small loss of alkali involves a substantial self-discharge.

b) The water content of the alkali in the cell steadily evaporates on the large, porous surface of the cathode both in use and out of use. This effect also tends to lower the alkali level which leads to the oxidation of the zinc electrode and to a decrease in the ampere-hour capacity of the cell. In order to eliminate this effect a separate water container is required, with separate tubings to feed water into the individual

cells. This solution is, however, complicated and still does not provide a sufficient control of the system, since the alkali level is reduced not only by vapourization but also by failures in sealing, too, as discussed above. Thus, after a certain period of operation, the alkali content of the cell becomes more concentrated or more dilute than required, reducing both the output and the life of the cell.

c) In order to prevent the alkali from forming carbonates a closed cell, provided with a carbon dioxide filter and fan, must be used. This arrangement is, however, practically useless for small cells, since the operation of the auxiliary equipments would require more energy than that supplied by the cell.

This invention aims at providing metal-air hybrid fuel cells, which are free of the disadvantages of the known ones, produce the same or higher specific energy, contain electrodes with essential unchanged properties during cyclical use, and thereby have a long life.

Now it has been found that an improved metal-air hybrid fuel cell may be provided if the electrode sequence is reversed, that is, the cathode is arranged in the space between the anodes in the separate cell casing, and the cathode is made removable. This discovery is very surprising, since on the basis of the state of the prior art one might expect that the specific energy of the cell would be lower owing to the use of a separate cell casing.

This invention is based further on the discovery that if the cathodic element or portion is placed within the anodic element or portion, the thickness of the anode can be decreased, thereby increasing the ampere-hour efficiency of the cell.

Accordingly, this invention consists in a metal-air hybrid fuel cell comprising a metallic anodic portion which defines an internal space for electrolyte, and a cathodic portion which is so mounted inside the electrolyte space as to be readily removable from said space independent of the anodic portion.

Optionally there are two anodes constituting the anodic portion, each having a thickness of 0.2 to 2 mm.

Thus the cathode of the cell embodied in the invention, in contradistinction to the known designs, is not used simultaneously as the cell casing. The electrodes are arranged in a separate casing, and, instead of the anode, the cathode is exchangeable or replaceable. From this arrangement it follows that when a cell is discharged, the anodic portion is left in the cell and is charged directly in this position by removing the cathode and substituting for it an auxiliary or charging electrode. In a multi-cell arrange-

ment, the cathodes may be removed either separately or together, if mounted on a common lid. The or each auxiliary electrode may be installed and replaced in the same manner. When the cathodes are removed jointly by virtue of being electrically connected to each other by the common lid, external connecting wiring becomes unnecessary.

A metal-air hybrid fuel cell according to the invention is described by way of example only, with reference to the annexed drawings, wherein:

Figure 1 is a sectional view of the cell according to the invention, but with the cathode removed, for the sake of clarity,

Fig. 2 is a side view of the cell shown in Fig. 1,

Fig. 3 is a sectional view of the cathode of the cell shown in Fig. 1, and

Fig. 4 is a sectional view of an auxiliary electrode used for charging the anodes of the cell shown in Fig. 1.

In Fig. 1 there are arranged two anodes 2 in a cell casing 1. The height of the electrolyte 4 is, in the absence of the cathode, at about the middle of the cell. The terminals 3 of the anodes are led out through openings 5 of the cell casing 1. Separators 6 are arranged adjacent the anodes 2. Rubber seals 11 ensure fluid-tightness for the anode terminals 3.

The cathode shown in Fig. 3 is made of a metal powder, preferably silver or platinum powder, pressed on a metal screen, preferably a nickel screen. In Fig. 3 the metal screen together with the metal powder is designated as plate 7. The cathode is made of two plates 7 so that the two plates are inserted into a frame 8 surrounding both plates 7. The upper part 8a of this frame serves at the same time as the cell cover. The upper part 8a of the frame 8 is provided with rubber sealing 10 for ensuring fluid-tightness between the cell casing and the frame part 8a. The cathode terminal 9 is led out through a corresponding opening of the frame part 8a; this opening is not shown. Air exchange of the cell takes place through an opening 10'.

The auxiliary charging electrode shown in Fig. 4 has the same form as that of the cathode, that is, it is arranged in a frame 12 of the same form as that of the cathode. This electrode is generally made of iron plates 13. The terminal 14 of this electrode is arranged in the same way as that of the cathode.

The cathode as shown in Fig. 3 can be put into the cell shown in Fig. 1 by simply immersing the cathode into the cell casing shown in Fig. 1 until the rubber seal 10 abuts against the edge 15 of the cell casing. The volume of the electrolyte should be such as to have an electrolyte level some milli-

metres above the top of the anodes 2 after arranging the cathode in the cell containing the anodes.

The main advantages of the hybrid fuel cell according to the invention are as follows:

a) It is not necessary to move the anode during charging, thus it is not subjected to mechanical strain, which results in an increased life.

b) During charging, the cathode is not immersed into the cell and exposed to its aggressive medium. The cathode can be stored in distilled water during charging and when the cell is stored, thereby substantially increasing the life of this electrode.

c) For cells with a zinc anode any dendrites formed during charging cannot short-circuit the system, since the cathode has been removed from the cell.

d) The level of electrolyte in the cell does not decrease appreciably, thus the direct oxidation (self-discharge) of the anode can be avoided.

e) Any alkali loss arising from the occasional leakage of the cathode can be compensated simply by refilling into the cell casing the alkali leaked into the well below the cathode. Thus the amount of the electrolyte is decreased only by the vaporization of water, the consequence of which can be eliminated easily and accurately by pouring distilled water into the cell. Consequently, the concentration of the electrolyte can be maintained at a constant level. Thus no water containers and water feed tubings are required to stabilize the concentration of the electrolyte and to supplement the water losses.

f) No alkali losses occur during cyclic operation, (charging and discharging) since only a negligible amount of alkali is removed by the cathode or the auxiliary electrode during removal and reinstallation.

g) As internal charging is possible, a separate apparatus, required for the external charging of the anodes, is unnecessary.

h) Cathodes can be arranged on a com-

mon lid, whereby the cathodes of several cells can be removed or reinstalled simultaneously, practically within some minutes.

i) The narrow opening for air supply between the cathodes enables the use of simple methods to filter out carbon dioxide in the air supply for small cells as well.

j) The arrangement of cathodes according to the invention allows an increase in the specific capacity of the anode, since anodes of lower mechanical strength, i.e. of greater porosity can also be used. Thus an increase in load can be achieved without a simultaneous decrease in life.

The design and the operation of the metal-air hybrid fuel cell according to the invention is further elucidated with the aid of the following Example:

Example

Two cells of 400 watt-hour capacity were constructed from zinc anodes of 100×125 mm. dimension and an oxygen cathode of 100×125 mm. dimension, prepared of silver powder bonded to a nickel screen and rendered waterproof with polytetrafluoroethylene. The cathode was coated with silver catalyst. The separators consisted of Cellophane (registered Trade Mark) sheets. 30% potassium hydroxide was used as electrolyte.

One of these cells was constructed in the conventional way, that is, the casing of the cell was formed by the cathodes, and the anodes were placed inside this casing.

The second cell was constructed according to the invention, that is, the anodes were placed into a separate cell casing and the cathodes were situated between the anodes.

The anodes of the cell with the conventional construction were charged externally. The cell constructed according to the invention was charged by means of an auxiliary electrode, as described.

The characteristic data of the cells are compared with each other in the following Table.

TABLE

	External charging (conventional cell)	Internal charging (cell according to the invention)
Number of cycles (zinc electrode)	46	93
Number of cycles (oxygen electrode)	153	340
Electrolyte losses during 100 cycles of charging and discharging	30%	5%

WHAT WE CLAIM IS:—

1. A metal-air hybrid fuel cell comprising a metallic anodic portion which defines an internal space for electrolyte, and a cathodic portion which is so mounted inside the electrolyte space as to be readily removable from said space independently of the anodic portion.

2. A metal-air hybrid fuel cell according to claim 1, wherein an auxiliary electrode is provided for mounting in said space during charging and storage after the cathodic portion has been removed.

3. A metal-air hybrid fuel cell according to claim 1 or 2, wherein the anodic portion comprises two anodes, each having a thick-

ness of 0.2 to 2 mm, and there are separators between said anodes and the cathodic portion or auxiliary electrode.

- 5 4. A metal-air hybrid fuel cell substantially as herein described with reference to the Example.

5. A metal-air hybrid fuel cell substantially as herein described with reference to and as shown in the accompanying drawings.

T. Z. GOLD & COMPANY,
Agents for the Applicants,
Chartered Patent Agents,
Staple Inn Buildings North,
High Holborn,
London, WC1V 7QB,
and
2, Fawley Road,
London, NW6 1SH.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

1438203

COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale*

Sheet 1

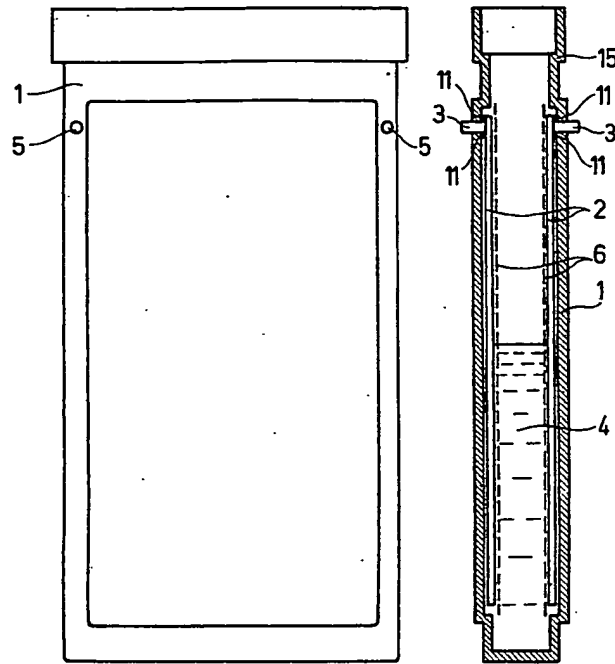


Fig.2

Fig.1

1438203

COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale
Sheet 2*

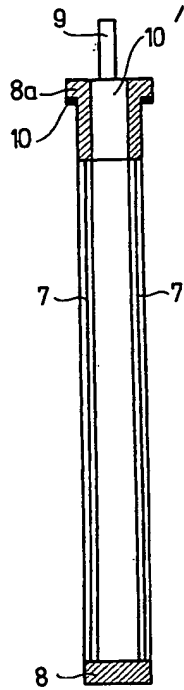


Fig.3

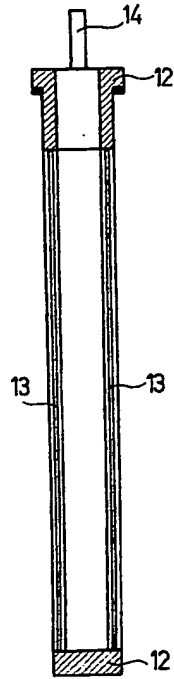


Fig.4